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CHROMATE ABATEMENT IN THE Y-12 PLANT'S NEW HOPE POND

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ABSTRACT

A 15-months field study has been completed that utilized four nonchromate-based water-treatment programs in 16 low-temperature (< 100° F) cooling towers using corrosion and deposition studies, microbiological control, and plant effluent creek analyses as evaluation parameters. The study succeeded in bringing the effluent of the New Hope Pond to the limits established by the Environmental Protection Agency.

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SUMMARY

Results from the New Hope Pond chromate-abatement study can be summarized as follows:

- 1. All four of the nonchromate-based water-treatment programs yielded very satisfactory results from the standpoint of corrosion. However, two of the programs yielded better results in controlling the problem of fouling.
- 2. The test heat exchanger, which operated at a temperature from 16 25 degrees Fahrenheit higher than that normally encountered in cooling water systems indicated that two of the treatment programs were better in the control of deposition.
- 3. Microbiological control proved to be the most difficult problem encountered in the evaluation. The microbiocides used in conjunction with two of the programs were ineffective in the control of algae and bacteria. A serious foaming problem was also encountered with one of the microbiocides; and, although a defoaming agent was added prior to injection of the microbiocide, foaming still was a problem.
- 4. Comparative analyses of the field control test kits and the Plant Laboratory analyses indicated good correlation in only two of the programs.
- 5. There was no environmental creek impact from the formulation of the materials insofar as cooling tower blowdown was concerned. However, substituting these materials for the chromate-based treatment had a two-fold environmental creek impact: (1) the effluent total chromium content was less than 0.05 ppm; (2) algae growth in New Hope Pond showed a significant growth increase due to the elimination of the chromate. This increase in algae growth has resulted in an effluent pH variance beyond the limit established. This variance occurs during the summer and early autumn months and is due to the algae which utilizes sunlight in its growth cycle, producing hydroxyl ions, resulting in the pH variance.
- The increase in cost reflected in the report by utilizing the more expensive nonchromate treatments is offset by the fact that the costly chromate destruction facilities are now not necessary.
- 7. All of the cooling-tower water systems in the Y-12 Plant have been converted to the nonchromate-based water-treatment programs utilizing microbiocides which do not create environmental creek impact. Inspection of many heat exchangers from the various cooling tower water systems reflect that adequate corrosion, deposition, fouling, and microbiocidal control is producing effective results.

INTRODUCTION

An environmental management appraisal was conducted by the AEC-ORO during. September 20 - 24, 1973. Pertinent sections of that appraisal concerning the chromate content in New Hope Pond are repeated here.

IV. Findings

G. The 1970 appraisal, transmitted February 19, 1971, stated "Y-12 should promptly perform a study of the economic impact of substituting a nonchromated corrosion inhibitor in or providing chromate recycling equipment for the cooling towers necessary to achieve assured conformance with this expected stream classification by FY 1974 and propose to ORO a phased and orderly plan for corrective action". Subsequently, the results of a three-month test (conducted prior to that appraisal) of a substitute made by Calgon produced what Y-12 felt were inconclusive results. The only other empirical investigative effort of which we have been made aware was a 12 - 18-month test on four Biology Division towers using another substitute. This test was conducted without monitoring and evaluation provisions until the final two months, and was judged by Y-12 to have produced undesirable results. While further testing of promising substitutes may be desirable, a more aggressive plan needs to be developed and implemented. It is expected that the EPA will issue a discharge permit for Y-12 sometime between June and December 1974, and that it will include a requirement to meet an 0.05 ppm chromium effluent limit. Between now and that time, all reasonable alternatives need to be seriously explored. Those include the use of a significantly lower chromium concentration in the cooling system, the use of softened make-up water, and the use of higher cycles of reconcentration.

III. Recommendations of the 1973 Appraisal

- C. Develop and implement a firm schedule to:
 - 1. determine which cooling tower systems do not require a chromated corrosion inhibitor, and
 - 2. empirically evaluate the use of:
 - a. significantly lower concentrations of chromium in those cooling towers requiring such treatment, and
 - b. a marked increase in the cycles of reconcentration through measures such as the use of softened water.

The study, which is the topic of this report, was conducted at the Oak Ridge Y-12 Plant (a) in conformance with these AEC-ORO recommendations.

⁽a) Operated by the Union Carbide Corporation's Nuclear Division for the US Energy Research and Development Administration.

STUDIES IN CHROMATE ABATEMENT

Y-12 COOLING TOWER WATER SYSTEMS

Cooling Tower Identification

The cooling towers employed at Y-12 are identified by the following numbers: 9409-2, 9409-3, 9409-4, 9409-6, 9409-10, 9409-12, 9409-13, 9409-15, 9409-16, 9409-17, 9409-18, 9409-19, 9409-22, 9409-23, 9409-24, 9409-26, 9409-27, 9409-28, 9409-29, 9409-30, 9409-31, 9409-32, 9409-33.

Capacity and Construction

The following facts describe the capacity and type of construction for the cooling towers:

- 1. Circulation rates range from 1500 to 27,800 gpm.
- 2. Total capacity, based upon heat rejection, is 9.5×10^8 Btu/hr at the full design heat load.
- 3. Air flow is by induced draft fans and estimated to be 18.9×10^6 cfm.
- 4. Materials of construction consist of untreated and Erdalith-treated redwood and douglas fir, cement asbestos board siding, silicon bronze fasteners and connectors, and mild steel distribution piping.

Process Cycle

Processing capabilities of the cooling towers can be summarized as follows:

- Makeup water to the cooling towers, to maintain the cycles of concentration at 3.0, can be either raw lake water or potable water, depending on the degree of turbidity of the raw lake water. The makeup flow rate at the cooling tower design heat load is 2750 gpm.
- 2. The cooled 85° F water in the cooling tower basin flows through 1/4-inch-mesh screens to the pump wet well. The water is pumped through mild steel pipelines to the building or buildings serviced and through various types of heat-exchange equipment. The 95° F water is then returned to the cooling tower distribution system. The tower distribution system breaks the water into small droplets which fall either counter current or cross current to the air flow being pulled into the tower by the induced draft fans. The water is cooled by the difference in the air temperature (sensible heat) and by evaporation (latent heat).
- 3. Side-stream sand filters are installed on some cooling towers (9409-13, 9409-18, and 9409-31). Approximately 1% of the recirculating water flow is passed through these filters to remove suspended particulate materials. Mechanical filters are used in several cooling tower systems to remove particulate matter.

4. Data pertaining to cooling tower water volumes, circulation rates, design characteristics, and operating conditions are reported in Table 1.

Table 1
COOLING TOWER DATA

Т	Volume	Volume	Circulation Rate	Rate Evaporation(1)	Drift Loss(2)	Blowdown(3)	Desi	gn(4)	(O F)
Tower Number	(gal x 10 ³)	(lbs × 10 ³)	(gpm x 10 ³)	(gpm)	(gpm)	(gpm)	WB	ST	RT
9409-2	225	1,876	6.0	60	0.5	30	78	85	95
9409-3	160	1,334	15.5	155	1.0	73	78	85	95
9409-4	225	1,876	27.8	334	1.5	167	78	88	100
9409-6	50	417	2.6	26	0.2	13	78	85	95
9409-10	85	709	9.0	90	0.5	45	78	85	95
9409-12	204	1,701	8.5	85	0.5	43	78	87	97
9409-13	250	2,085	25.5	255	1.5	128	78	87	97
9409-15	35	292	3.0	39	0.5	20	78	85	98
9409-16	35	292	3.0	39	0.5	20	78	85	98
9409-17	30	250	5.4	54	0.5	27	78	85	95
9409-18	80	667	9.5	95	0.5	46	78	85	95
9409-19	100	834	7.2	72	0.5	36	78	85	95
9409-22	110	917	5.4	54	0.5	27	78	86	96
9409-23	60	500	8.0	80	0.5	40	78	90	100
9409-24	90	750	7.6	76	0.5	38	78	85	95
9409-26	25	208	9.0	90	0.5	45	78	85	95
9409-27	18	150	4.2	42	0.5	21	78	85	95
9409-28	25	208	3.0	30	0.5	15	78	85	95
9409-29	25	208	6.0	60	0.5	30	78	85	95
9409-30	15	125	3.0	30	0.5	15	78	85	95
9409-31							78	85	95
9409-32	30	250	6.0	60	0.5	30	78	85	95
9409-33	15	125	1.5	15	0.5	8	78	85	95

⁽¹⁾ One percent circulation each 10 degrees change in temperature.

New Hope Pond Effluent Guidelines

The following chemicals and their respective limits have been set, based on Environmental Protection Agency (EPA) and State of Tennessee effluent limits: total chromium, 0.05 ppm; total phosphorus, 1.0 ppm; total zinc, 0.1 ppm; total phenol, 0.001 ppm.

Creek impact due to cooling tower blowdown water is as follows:

1. Blowdown to creek with three cycles of concentration and heat loads of:

⁽²⁾ At 0.005%.

⁽³⁾ Three cycles.

⁽⁴⁾ WB - wet bulb temperature; ST - supply temperature; RT - return temperature.

2. Chromate to creek (treatment level, 20 ppm) with three cycles of concentration and heat loads of:

100% = 116.49 lbs/day

 $75\% = 87.37 \, \text{lbs/day}$

50% = 58.25 lbs/day

 $25\% = 29.12 \, \text{lbs/day}$

3. Chromate above creek limits:

Creek Flow	Chromate Limits		omate per D Tower Blov	•)
(gal/day x 10 ³)	(ppm)	100% HL(1)	75% HL	50% HL	25% HL
5000	0.05	2.79	2.09	1.40	0.70
5250	0.05	2.66	1.99	1.33	0.66
5500	0.05	2.54	1.90	1.27	0.63
5750	0.05	2.43	1.83	1.21	0.60
6000	0.05	2.33	1.75	1.16	0.58
6250	0.05	2.23	1.68	1.12	0.55
6500	0.05	2.15	1.61	1.07	0.53
6750	0.05	2.07	1.55	1.03	0.51
7000	0.05	1.99	1.50	0.99	0.49

⁽¹⁾ HL - heat load.

WATER TREATMENT EVALUATION

Chromate-Based Water Treatment

The chromate-based water-treatment program utilized in the Y-12 Plant cooling-tower water systems is referred to as "zinc dianodic". The following is a brief summation of this treatment:

The zinc-dianodic formulation consists of chromate, polyphosphate, and zinc. In conjunction with this treatment, sulfuric acid is used to reduce the scaling tendency of the calcium bicarbonate in the makeup water by adjusting the pH to a mean value of 6.0. The reaction of calcium bicarbonate and sulfuric acid results in the formation of the more stable and more soluble calcium sulfate.

The acid-zinc dianodic water treatment results in a very slight film formation of zinc phosphate, which allows excellent heat transfer but stifles corrosion. This film formation protects base metals while the chromate prevents excessive pitting action.

The chromate in this treatment also aids in the control of fungal decay in wooden cooling towers. Redwood and douglas fir lumber are treated by the chromated copper arsenate (CCA) pressure treatment prior to installation. Also utilized in the

water treatment program is a biocide containing sodium pentachlorophenate. This chemical is "shock fed" into the water system to control algae, slime, and fungus. The following amounts are able to maintain the basic control for this treatment: chromate, 20 - 25 ppm; zinc, 2.5 ppm; phosphate, 1.8 ppm; pH (range), 5.8 - 6.2; biocide (phenol), 50 ppm.

From the standpoint of saving metal by providing a high degree of corrosion protection, the most effective corrosion inhibitors in use involve one or more of the chromate salts. In comparison with a system operating with water under a no-treatment condition, corrosion rates on metal surfaces can be reduced 95% when employing chromate-based inhibitors. An evaluation of the zinc dianodic treatment during 1964-1965 indicated corrosion rates on steel coupons to be less than 2.0 mils per year (mpy) and on copper coupons to be less than 0.5 mpy (1 mil = 0.001 inch). Corrosion rates of any water treatment determined to be negligible are 5 mpy on steel and 1 mpy on copper. From 10 to 20 mpy on steel is moderate and above 20 mpy is excessive.

The zinc dianodic water treatment was originally introduced into the gaseous diffusion plant water systems, where extremely high water temperatures have been experienced (140 - 185° F) and corrosion rates were accelerated. Introduction of this treatment into the Y-12 Plant cooling-water systems was based upon the fact that the treatment was extremely effective against corrosion and deposition, and it was relatively economical even though the corrosion rates and water temperatures in the Y-12 systems were low when compared to those at the gaseous diffusion plants.

The chromate-based corrosion inhibitor and phenol-based microbiocide are excellent from the standpoint of corrosion, deposition, and microbiological growth, but they do present a significant problem in pollution control of the water leaving the Y-12 New Hope Pond. The proposed maximum allowable stream limit has been established at 0.05 ppm total chromium and 0.001 ppm total phenol. Analysis of the creek indicates concentrations from 0.10 to 0.45 ppm total chromium without the towers at their full design heat load. Even if all uncontrolled blowdown is stopped from the cooling tower systems, the normal blowdown from the towers, if they are loaded to design conditions and controlled at three cycles of concentration, would still exceed the proposed 0.05 ppm total chromium and 0.001 ppm total phenol effluent limits.

Proposed Treatment Evaluation

A steering committee and an "ad hoc" working committee were established at the Y-12 Plant to investigate and evaluate the use of nonchromate-type corrosion inhibitors to alleviate the pollution problem. It was anticipated at this time that the evaluation of the various treatments may indicate it would be necessary to sacrifice some metal corrosion in order to substitute the nonchromate inhibitors. Corrosion and deposition rates were to be established to determine the degree of deterioration. In order to make this investigation, the following program was outlined:

 Utilities personnel would eliminate all uncontrolled blowdown from the water systems as soon as practicable.

- 2. The ad hoc committee would contact water-treatment companies and request proposed treatments for the type of water and temperatures involved. All the companies would provide corrosion test coupons and test heat exchangers at no cost to Y-12.
- Members of the ad hoc committee would visit other industrial facilities where nonchromate water treatments have been evaluated over the past three to four years.
- 4. Creek samples would be analyzed for chromate.
- The ad hoc committee would direct its activity to the substitution of a nonpolluting biocide for the existing phenol-base inhibitor since a proposed effluent limit of 0.001 ppm phenol had been established.
- 6. Corrosion test coupons, resistance probes, and test heat exchangers would be used to monitor the corrosivity and deposition experience with the new water treatment programs.
- 7. Creek samples and compilation of creek data would be obtained throughout the program.
- 8. Corrosivity and deposition studies would be obtained throughout the program.
- 9. Creek-sample analyses and field and laboratory methods to control the various water-treatment programs would be obtained.
- 10. The evaluation would be performed during the period from January to October 1974.

Cooling towers involved in the evaluation of the water-treatment methods are listed, with their design characteristics, in Table 2.

Towers 9409-13, 9409-26, 9409-24, 9409-18, and 9409-31 were not included for the test program since the processes and equipment served by these towers were more susceptible to damage should deposition occur. Corrosion and deposition rates would be established on the new treatments before the program was extended to these towers.

During the month of December 1973, the zinc dianodic treatment was phased out of the towers used in the investigation. The new water-treatment systems were initiated into the towers shortly after the first of January 1974.

Treatment Changeover

During the changeover from the chromate to the nonchromate treatments, the towers were taken out of service one at a time. All chromate-treated water in the basins was dumped to the sewers. This procedure eliminated the necessity for the step-wise pH adjustment and high inhibitor concentration levels. Towers that could not be shut down and drained were diluted by the addition of makeup water and allowed to overflow until the chromate residual was less than 1 ppm. Creek samples were obtained during the dumping procedure and analyzed for environmental impact to the creek.

The data in Table 3 indicate the creek impact from draining the cooling towers.

Inspection of Equipment

Several heat exchangers that had been exposed to the chromated water treatment and the straight phosphate treatment in the Biology Area were inspected on the water side.

A view of the inlet and outlet sides of the two-pass air-conditioning heat exchanger for one of the Biology buildings, that has been in service three years on the chromate treatment, is presented in Figure 1. As seen, scaling was primarily on the outlet of the tubes and consisted primarily of iron hydrate and some chromium oxide. Of the 460 tubes, 72 were plugged mostly from "chunks" of redwood from the cooling tower. Figure 2 gives a view of the opposite end of the heat exchanger. The formation of iron hydrate and chromium oxide indicates the system has been at low pH (< 5.0) for some period of time.

Figure 3 is a view of the Gardiner-Denver air compressor intercooler heat exchanger. This unit had been in service 11 months and 15 days since the last cleaning period. Twenty-seven percent of the deposition in this heat

Table 2
TOWERS INVOLVED IN THE EVALUATION STUDY

Tower Number	Volume (gal x 10 ³)	Circulation Rate (gpm × 10 ³)	Makeup Rate (gpm)				
	Gro	up A					
9409-22 9409-23 9409-27 9409-33	110 60 18 15 203	5.4 8.0 4.2 1.5	81.5 120.5 63.5 23.5 289.0				
	Gro	рир В					
9409-19 9409-28 9409-29 9409-32 9409-30	100 25 25 30 15 195	7.2 3.0 6.0 6.0 3.0 25.2	108.5 48.5 90.5 90.5 45.5 380.5				
	Gro	oup C					
9409-10 9409-12 9409-17	85 250 30 365	9.0 8.5 5.4 22.9	135.5 128.5 81.5 345.5				
	Group D						
9409-2 9409-6 9409-15 9409-16	225 50 35 35 345	6.0 2.6 3.0 3.0 14.6	90.5 39.5 54.5 54.5 239.0				

exchanger was due to biological fouling. The balance of the deposit consisted mainly of iron hydrate, chromium oxide, and silica (from mud). Figure 4 shows the heat exchanger head with similar deposits. The aftercooler tube bundle on this air compressor required acid cleaning to get the tubes clean.

The heat exchanger from the plant air compressor is seen in Figure 5. Although there was evidence of some biological fouling, the major constituent in the deposition was iron hydrate, followed by chromium oxide and silica. This heat exchanger had been in service approximately 11 months since the last cleaning. Figure 6 shows the head of this heat exchanger and indicates a very heavy deposition of iron hydrate.

A view of another air conditioning heat exchanger is presented in Figure 7. Wood chips had caused the plugging of 12 tubes. This unit was inspected approximately 2 1/2 months after initiation of the nonchromate treatment into the 9409-10 cooling tower. It was thought that a problem of maintaining load on the unit was due to heat-exchanger plugging, but this was not the case. There was a slight, soft, muddy deposit on the tubes which analyzed to be

iron hydrate, silica, chromium oxide, and carbon. The fact that the deposit was very soft, indicated that the new water treatment system was removing old deposits. The deposition was easily removed from the tubes with high-pressure air and then rinsed with clean water. The head of this heat exchanger is seen in Figure 8.

Figures 9 and 10 are photographs of a 250-ton air conditioner unit in the Biology Area. Cooling towers 9409-19, -28, -29, and -32 in this area had been treated with a straight phosphate treatment (sodium hexametaphosphate) and a pH adjustment with sulfuric acid during CY 1973. Test heat exchanger tube data had indicated a rather heavy deposit of tricalcium phosphate under these treatment conditions. Inspection of the 250-ton air conditioner heat exchanger unit bore out these test data. The "whitish" appearance of the deposition was analyzed to be tricalcium phosphate and could not be removed by air, water jet, or mechanical brushing. This type of deposition interferes with heat transfer.

Figures 11 and 12 show small heat exchangers removed from machines that are served by the 9409-27 cooling tower. Figure 11 shows the heads of the exchangers with an extreme

Table 3
CHROMIUM CONTENT OF CREEK SAMPLES

Day (11/73)	Time	Total Chromium (mg/I)	Hexavalent Chromium (mg/l)	Day (11/73)	Time	Total Chromium (mg/l)	Hexavalent Chromium (mg/I)
			***			9717	(119/1/
22	1:00 am	0.014		26	4:50 pm	0.062	
22	5:00 am	0.014		26	9:00 pm	0.020	
22	9:00 am	0.020		27	1:00 am		
22	1:00 pm	0.011		27	5:00 am	0.013	
22	5:00 pm	0.016		27 27		0.003	
22	9:00 pm	0.022		21	9:00 am	0.003	
23	1:00 am	0.051	0.050	28	12:55 am	0.004	
23	5:00 am	0.030	0.050	28	8:50 am	0.003	
23	9:00 am	0.028	0.025	28	3:30 pm	0.021	
23	1:00 pm	0.013	0.025	28	6:00 pm	0.095	
23	5:00 pm	0.032		28	10:00 pm	0.800	
23	9:00 pm	0.032		29	0.00		
	_	0.028		29 29	2:00 am	0.003	
24	1:00 am	0.028			6:00 am	0.002	
24	5:00 am	0.006		29	10:00 am	0.019	
24	9:00 am	0.025		30	1:30 am	0.120	
24	1:00 pm	0.042		30	9:30 am	0.033	
24	5:00 pm	0.190	0.173				
24	9:00 pm	0.022		(12/73)			
25	1:00 am	0.024		_			
25	5:00 am	0.030	0.030	5	4:30 am	0.053	
25	9:00 am	0.010		5	8:15 am	0.024	
25	1:00 pm	0.022		5	11:45 am	0.029	
25	5:00 pm	0.021		6	2:00 am	0.023	
25	9:00 pm	0.013		6	6:00 am	0.023	
20	4.00			6 ′	10:00 am	0.032	
26 26	1:00 am	0.019	0.015	6	2:15 pm	0.030	
26 26	5:00 am	0.019		6	6:00 pm	0.036	
26	8:40 am	0.008			·		
26	9:40 am	0.017		7	6:00 am	0.021	
26.	12:00 pm	0.013		7	9:30 am	0.021	

deposition of iron hydrate and chromium oxide; Figure 12 shows a heat exchanger with one of the corroded copper tubes removed from the tube bundle. The heavy deposition in the heads and corrosion of the copper tubes was caused by loss of pH control in the cooling water system.

Two views of an 800-ton air conditioner unit in the Biology Area are provided in Figures 13 and 14. These pictures were taken upon completion of the water treatment evaluation. The "whitish" tricalcium phosphate deposition has been removed and all of the tubes had an

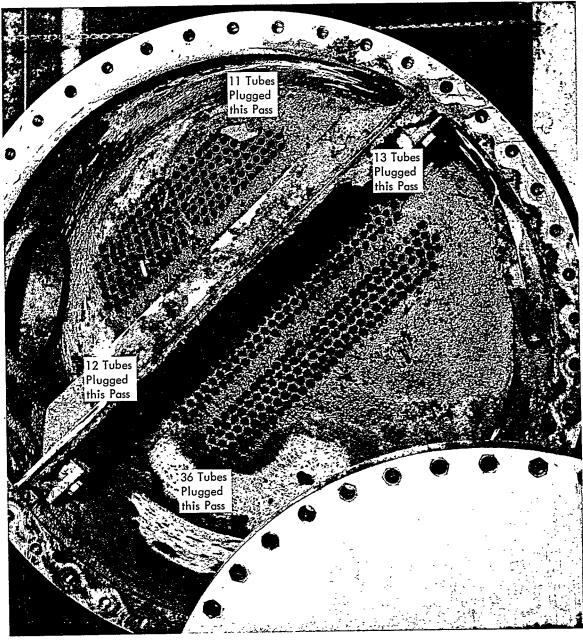


Figure 1. INLET AND OUTLET SIDES OF THE TWO-PASS HEAT EXCHANGER.

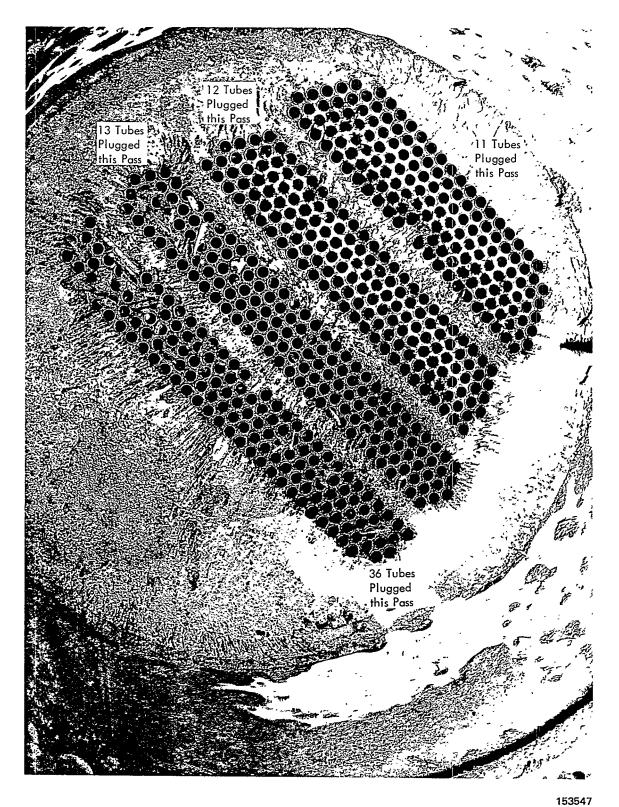


Figure 2. OPPOSITE END OF THE TWO-PASS HEAT EXCHANGER.

extremely clean, bright, copper appearance. The material observed in the water boxes was soft and muddy in appearance and very easily removed. The deposit was primarily iron hydrate and silica and had dropped out in the low-velocity area of the water boxes.

An analysis of deposits from the heat exchangers is reported in Table 4.

Corrosion-Deposition Studies

The relative corrosivity of the cooling-tower water was determined by measurement of the weight loss of uninhibited metal specimens inserted in the cooling-tower return water systems. The steel and copper metal specimens were supplied by the water-treatment consultants/suppliers of the formulations under evaluation. The weighing and evaluation was also performed by the consultants/suppliers.

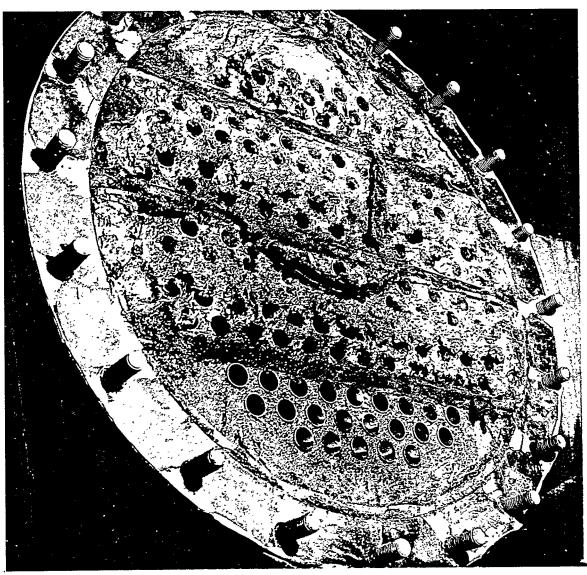


Figure 3. INTERCOOLER ON THE GARDINER-DENVER AIR COMPRESSOR.

Corrosivity measurements in recirculating cooling water obtained by the use of metal specimens do not give precise values of the corrosion to be expected on metal surfaces in the system. Such measurements do give a figure for the corrosion rate of the metal under the conditions tested, which is useful for comparative purposes. This advantage is especially true when determining if the corrosion-inhibitive treatment being used in the system is giving adequate control. Examination of the specimens can also give an indication of pitting tendencies and scaling or deposition.

Metal specimens were cleaned and weighed to the nearest tenth of a milligram prior to insertion in the cooling water systems. They were mounted on plastic or fiberboard rods and inserted in a specimen-holder assembly. Water flow over the specimens was maintained at rates from 3 - 6 ft/sec. A total of 12 specimens were in each assembly—6 steel and 6 copper. Each 30 days, one steel and one copper specimen were removed for corrosion and deposition analysis and new specimens inserted in their places.

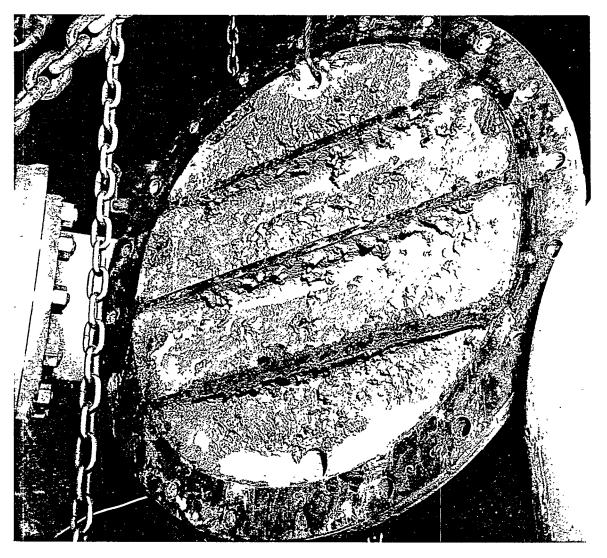


Figure 4. HEAD OF THE GARDINER-DENVER AIR COMPRESSOR.

The following facts were recorded on each specimen:

- 1. Identification of the cooling system.
- 2. Identification of the specimen.
- 3. Type of metal specimen.
- 4. Duration of the test.
- 5. Flow rate of the water.
- 6. Weight loss of specimen.
- 7. Average corrosion rate in mils/yr.
- 8. Appearance of the specimen before and after cleaning.

The average corrosion rates obtained during the test period for each treatment evaluated are listed in Table 5.

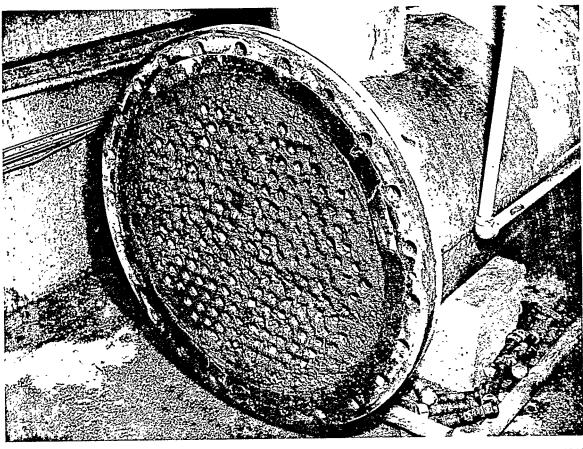
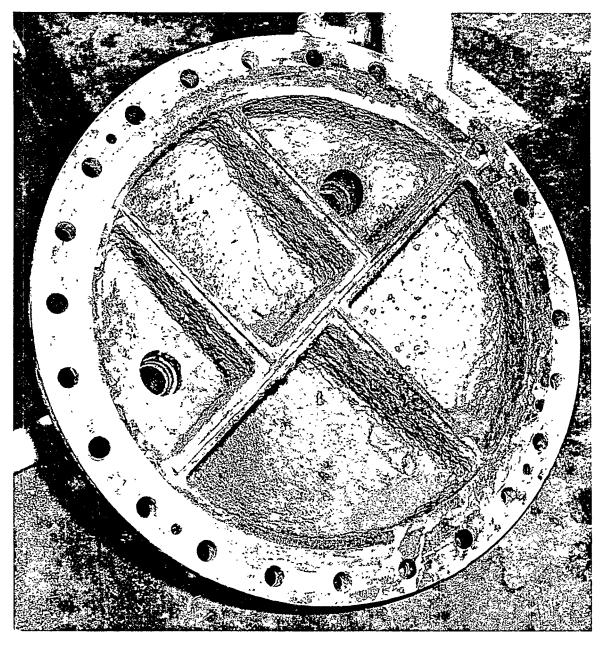


Figure 5. PLANT AIR COMPRESSOR INTERCOOLER.

Table 6 gives a more detailed report on the corrosion data. All materials were satisfactory with regard to corrosion. The phosphonates are normally corrosive to copper and copper alloys. Mercapto benzol thiazole was formulated with the phosphonates which protected the copper, as the data indicate.

"Fouling" refers to loose, porous, or gelatinous deposits of insoluble salts, adhering hydrous oxides produced by corrosion, and such other foreign materials as dirt, carbon, chromium, and calcium salts. All systems inspected indicated the presence of fouling. Reference is made to the preceding section, **Inspection of Equipment**.



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Figure 6. HEAD OF THE PLANT AIR COMPRESSOR.

Of the four water-treatment corrosion/deposition inhibitors evaluated, B-CDI and C-CDI indicated superior results in controlling fouling. The previous sodium hexametaphosphate treatment utilized in the Biology cooling system coated the system with tricalcium phosphate. After introduction of the B-CDI treatment, the phosphate concentration in the cooling-tower water increased significantly for approximately one month, indicating that the systems were being cleaned on stream.

The C-CDI material was utilized in the 9409-10 cooling tower system. In approximately two months, a substantial accumulation (4 - 6 inches) of fouling products (carbon, iron hydroxide, silica, and chromium) was found in the cooling-tower basin. The basin had been drained and washed with hoses before C-CDI was initiated. It was drained and cleaned upon observing the accumulation of fouling products in the basin. Inspection in October again showed a heavy accumulation in the basin, further indicating on-stream cleaning.

The metal-specimen test procedure gives an overall corrosion rate, but will not yield instantaneous results. Resistance-type probes provide instantaneous corrosion rates by

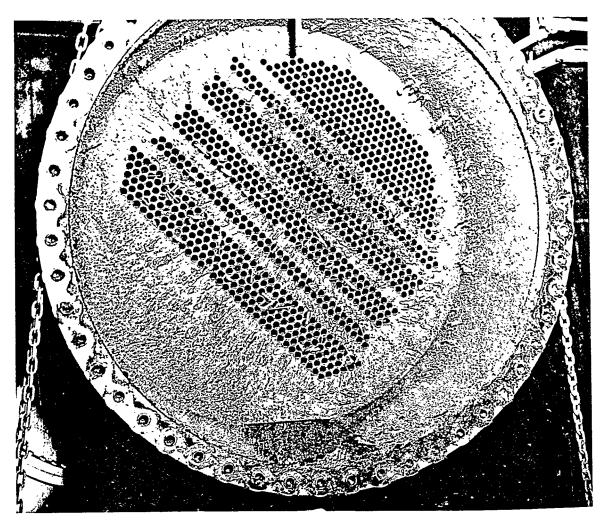


Figure 7. HEAT EXCHANGER FOR A BIOLOGY AIR CONDITIONER UNIT.

measuring the potential difference between a steel test electrode and a reference electrode. Resistance probes were installed on a cooling-tower system from each of the four test groups and were used for routine spot checks on the corrosivity of a system by leaving them in each system continuously and making scheduled measurements. The instrument used in conjunction with the probes was the Magna Corrator. (b) In general, the instantaneous corrosion rates obtained were lower than rates obtained by the metal specimens. The Corrator also provides a measurement of the pitting tendency of the cooling water.

The results obtained by the resistance-probe corrosion method are summarized in Table 7.

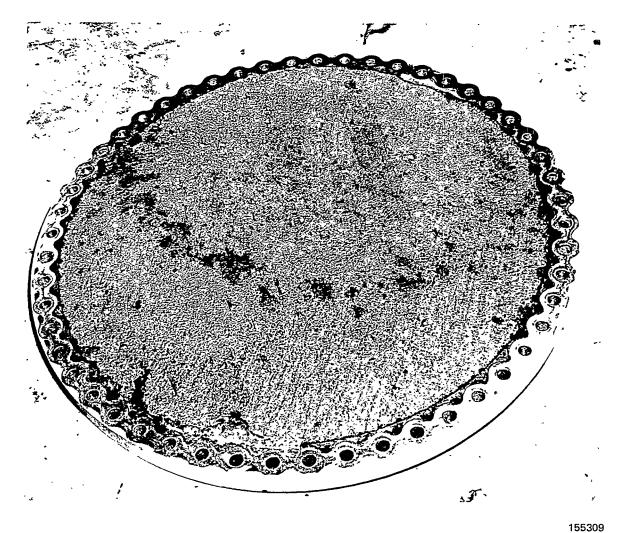


Figure 8. HEAD OF THE BIOLOGY AIR CONDITIONER UNIT.

⁽b) A product of the Magna Corporation, Santa Fe Springs, California.

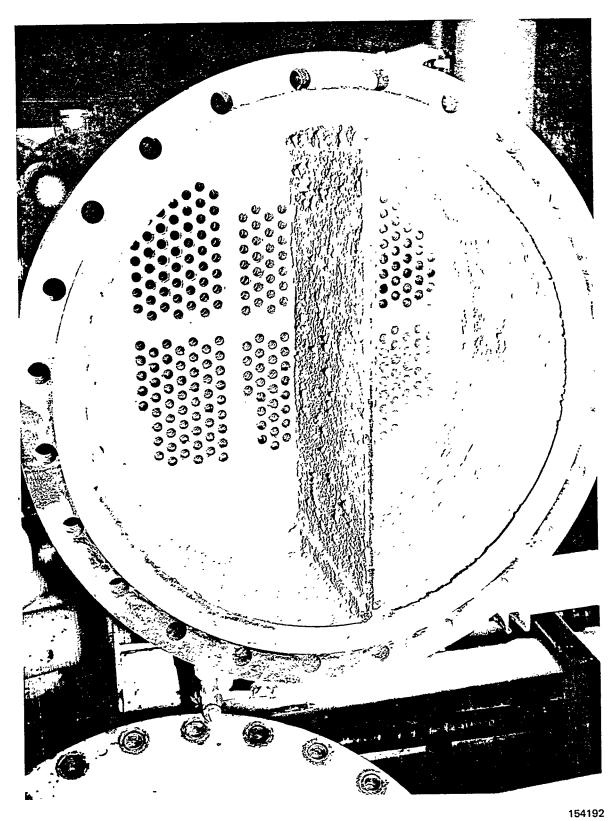


Figure 9. AIR CONDITIONER UNIT, SHOWING A HEAVY CALCIUM PHOSPHATE DEPOSIT. (250-Ton Unit)

Heat Exchanger Data

A small test heat exchanger containing steel tubes was installed on one cooling-tower water system in each of the four groups of towers under evaluation. The flow was maintained at a rate between 4 and 5 ft/sec, and the water temperature was elevated from 16 to 25° F by using 10-psig steam. Heat-transfer coefficient data obtained were inconclusive; however, examination of the tubes, the type of deposition, and examination for pitting after removal of the deposition indicated that Treatments B-CDI and C-CDI were superior to the other treatments. The deposition in these tubes was very thin, easily removed, and there was no evidence of excessive pittings in the tube walls.

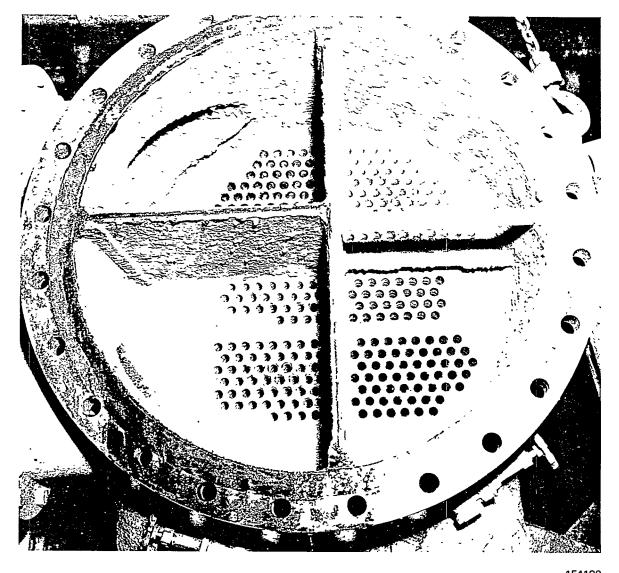


Figure 10. ANOTHER VIEW OF THE HEAVY DEPOSIT OF CALCIUM PHOSPHATE ON THE 250-TON AIR CONDITIONER UNIT.

Microbiological Tests

Microbiological control proved to be the most difficult problem encountered in this evaluation. The microorganisms that were closely monitored were bacteria and algae.

No attempt was made to analyze the water for the presence of fungi which can destroy the wood in a cooling tower. No materials in this evaluation nor those used in the chromate/phenol treatment would control fungi in the sections of the cooling tower where the water does not circulate (the drift eliminator and plenum areas). Control of these microorganisms is best accomplished by taking the tower out of service and spray treating those areas where the water does not circulate or by steam sterilization.

Algae is present in most soils; and, when dust enters the tower, it brings algae. Most algae in cooling towers are blue-green or green in color and must have sunlight, carbon dioxide, and

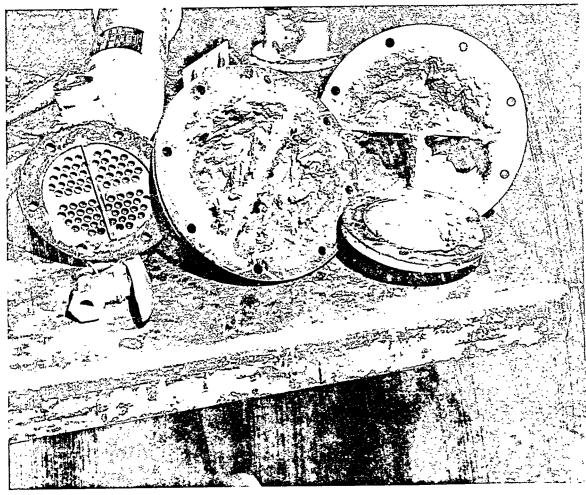


Figure 11. HEADS OF SOME SMALL HEAT EXCHANGERS.

a few minerals for survival. Effectiveness of the microbiocides to control algae was evaluated by visual observation of the plenum chambers, fill areas, and open distribution decks on the cooling towers to determine if algae growth was evident. A program was initiated during this evaluation to cover the open basins on two cooling towers and the open distribution decks on 11 cross-flow cooling towers. This covering greatly reduced one of the necessities for algae growth—sunlight. Visual inspection of these towers since installation of the covers and application of a proper dose of the proper microbiocide shows practically the elimination of algae growth.

Effectiveness of the microbiocides to control bacteria was evaluated by an American Petroleum Institute procedure utilizing broth bottles. Bacteria enter the tower primarily via the air stream and it was essential that bacterial control be maintained since inspection of many heat exchangers had shown biological fouling. The two types of bacteria evaluated were: (1) aerobic bacteria (those that need oxygen to grow), and (2) anaerobic bacteria (those that do not need oxygen for growth). An example of aerobic bacteria is "iron bacteria" that oxidize ferrous iron to ferric iron. An example of anaerobic bacteria is "sulfate-reducing bacteria" that cause corrosion by producing hydrogen sulfide and ferrous sulfide.

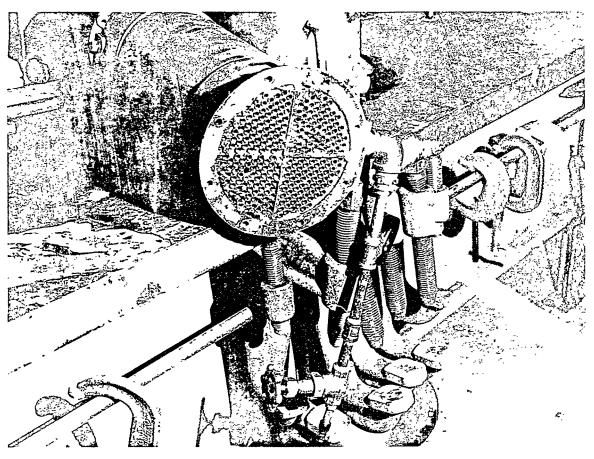


Figure 12. HEAT EXCHANGER WITH A CORRODED COPPER TUBE REMOVED.

Inoculation of the broth bottles was performed directly at the cooling tower using sterile syringes. This procedure alleviated the necessity for sterile sample bottles and the possibility that the sample could be contaminated.

Most all water-treatment suppliers provide microbiological analysis service at no cost. However, some of these results can be questionable. When samples are held for a few days in transit, all anaerobes die; the fast-growing species sometimes crowd out the slow-growing species; and, if a microbiocide is present when the sample is taken, the results are grossly affected. Results of the bacteria analyses are listed in Table 8.

Results obtained by the bacteria test indicated that microbiocides B-MB and C-MB were satisfactory to control growth. Microbiocides A-MB1 and A-MB2, on the other hand, were

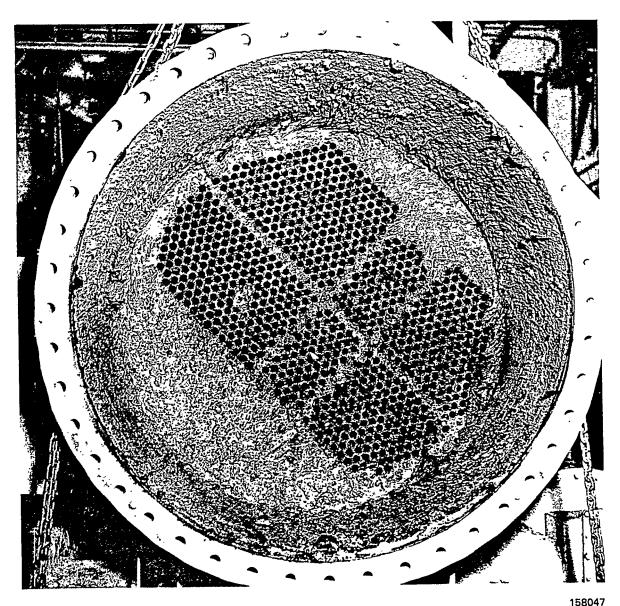


Figure 13. AN 800-TON AIR CONDITIONER UNIT WITH THE CALCIUM PHOSPHATE DEPOSIT REMOVED.

found to be unsatisfactory; in fact, the biological plugging of many heat exchangers occurred and each one had to be cleaned mechanically. These microbiocides also presented a foaming problem and required addition of a defoamer 10 minutes prior to the addition of the microbiocide.

Microbiocides D-MB1 and D-MB2 indicated good bacteria control; however, a filamentous algae growth occurred, not necessarily dependent on sunlight in three of the four test towers. The algae plugged the nozzles on one tower which required the water to be shut off and the algae removed. The pH of one system was lowered to 7.0 and sodium hypochlorite was used to retard the algae growth.

Although Microbiocides B-MB and C-MB proved to be the most effective, if they are used in a heavily infected system ($>10^6$ counts/ml) individually, a problem occurs in bringing the system under control. This problem is thought to be caused by an acclimation of the bacteria to the one microbiocide. By alternating these microbiocides in a system and employing a "double shock" treatment, control is usually obtained without further problems.

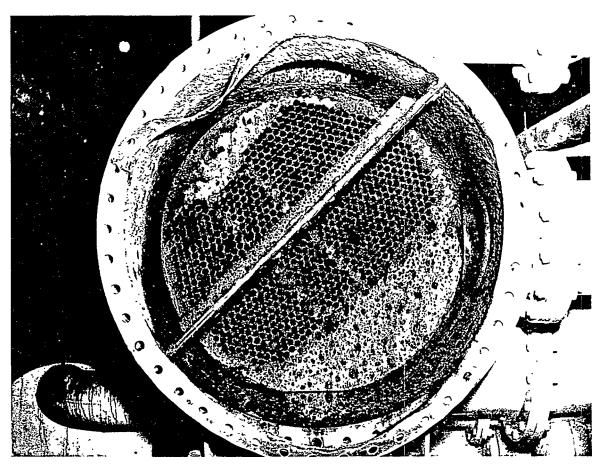


Figure 14. ANOTHER VIEW OF THE 800-TON AIR CONDITIONER UNIT.

Field and Laboratory Analyses

All consultant/suppliers recommended field test kits and supplied procedures for such kits whereby the operators could determine daily the corrosion/ deposition inhibitor levels in the cooling-tower water systems. These test kits were devised in a cookbook manner, were relatively simple to use, and took a minimum period of time (usually around 10 minutes on an average). Plant Laboratory personnel were utilized to train all the coolingtower-water-system operators in the use of the test kits. A comparison between values obtained by the field test kits and Plant Laboratory analyses was made and indicated good correlation, except for problem areas in some of the test kits.

The field test kit for Formulations A-CDI1 and A-CDI2 presented problems with the "factors" used for conversion to actual product level. This difficulty resulted in several analyses by the Plant Laboratory to determine the actual values of these factors.

Table 4
ANALYSIS OF DEPOSITS FROM SEVERAL HEAT EXCHANGERS

Sample Source	Analysis
Air Conditioner Unit (500 ton)	43.6% iron, 4.5% chromium, 1.2% silicon, and traces of copper, calcium, magnesium, manganese, and titanium.
Gardner-Denver	26.5% iron, 5.9% chromium, 2.0% silicon, and traces of copper, calcium, magnesium, manganese, and titanium; 26.9% LOI.(1)
South Carrier	silica (mud), iron hydroxide, and iron oxide.
Machine Heat Exchanger	iron tin hydroxide, iron chromate hydroxide, iron oxide hydroxide, and copper oxide.
Air Compressor	26.95% iron, 3.85% chromium, and 0.04% zinc.
Evaporator	39,54% iron, 0.71% chromium, and 0.13% zinc.
West Air Conditioner Unit	iron oxide hydroxide.
Air Compressor	17.47% silica, 2.76% iron, 1.85% aluminum, 0.54% chromium, 1.9% carbon, and traces of calcium, magnesium, carbonates, and phosphates; 75% LOI.
Air Conditioner	10% iron, 4% silica, 1.5% aluminum, 0.7% copper, and 0.5% chromium; 30.88% LOI.

⁽¹⁾ LOI-loss on ignition. Percent reported is basically biological fouling.

The field test kits for Formulations B-CDI and C-CDI proved to be reasonably accurate and reliable when compared to Plant Laboratory analyses. The field test kit for C-CDI was found to be inaccurate during the first week of the program because of the wrong calibration of a

Table 5
AVERAGE CORROSION RATES

Corrosion/Deposition	Corrosion Rates (mpy)			
Inhibitor(1)	Steel	Copper		
A-CDI-1 and CDI-2	0.59	< 0.1		
B-CDI	0.38	< 0.1		
C-CDI	0.49	< 0.1		
D-CDI	0.84	< 0.1		

These inhibitors are vendor-supplied materials and are identified by codes only.

colormetric code wheel. This problem was immediately resolved.

The field test kit for D-CDI was not accurate enough for product-level control. The Plant Laboratory had to be utilized to perform all product-level analyses, which proved to be time consuming since they also had many problems with the Plant Laboratory procedure supplied by the consultant/supplier. The consultant/supplier offered a field test kit based upon the requirements

CORROSION RATES OF COOLING WATER Table 6

		Inhibitor Level	Average Corrosion	orrosion	Lowest C	Lowest Corrosion	Highest Corrosion	orrosion
Cooling	Corrosion/Deposition	as Product	Rate (mpy)	(ydı	Rate (mpy)	(mpy)	Rate (mpy)	npy)
Tower	Inhibitor Used ⁽¹⁾	(mdd)	Mild Steel	Copper	Mild Steel	Copper	Mild Steel	Copper
9409-22	A-CDI	08 - 09	0.4	< 0.1	0.1	< 0.1	1.1	< 0.1
9409-23	A-CDI	08 - 09	0.5	< 0.1	0.2	< 0.1	1:1	< 0.1
9409-27	A-CDI	08 - 09	0.7	< 0.1	0.1	< 0.1	2.2	< 0.1
9409-33	A-CDI	08 - 09	1.2	< 0.1	1.0	< 0.1	1.3	< 0.1
9409-19	B-CDI	120 - 147	0.3	< 0.1	0.1	0.0	1:1	0.1
9409-30	B-CDI	120 - 147	0.2	< 0.1	0.1	0.0	0.7	0.1
9409-30(2)	B-CD1	29	0.1	0.1	0.1	0.1	0.1	0.1
9409-28, -29	B-CDI	29	0.5	< 0.1	0.1	0.0	1.4	0.1
9409-10	CCDI	20	1.4	0.1	0.5	0.0	3.0	0.2
9409-12	CCDI	20	0.5	< 0.1	0.3	< 0.1	0.8	0.1
9409-17	CCDI	20	0.5	< 0.1	0.2	< 0.1	1.3	0.1
9409-2	D-CDI	32 - 64	1.1	0.1	9.0	0.0	1.4	0.2
9409-6	D-CDI	32 - 64	1.2	< 0.1	0.8	0.0	1.7	0.2
9409-15	D-CDI	32 - 64	0.4	< 0.1	0.1	0.0	0.5	0.1
9409-16	D-CDI	32 - 64	8.0	< 0.1	9.0	. 0.0	1.4	0.2

(1) These inhibitors are vendor-supplied materials and are identified by codes only. (2) Only four coupons have been evaluated.

Table 7
RESISTANCE-PROBE CORROSION DATA

	A-CDI1	& A-CD12	B-0	CDI	C-CI	OI(1)	D-0	CDI	
	-	Corrosion/Deposition Inhibitor (mpy)		Corrosion/Deposition Inhibitor (mpy)		Corrosion/Deposition Inhibitor (mpy)		Corrosion/Deposition Inhibitor (mpy)	
	General		General		General		General		
Test	Corrosion Rate	Pitting Tendency	Corrosion Rate	Pitting Tendency	Corrosion Rate	Pitting Tendency	Corrosion Rate	Pitting Tendency	
1	0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	NA	NA	
2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.15	0.15	
3	0.05	0.05	0.05	0.1	0.5	0.9	0.60	0.60	
4	< 0.05	0.05	< 0.05	< 0.05	0.9	0.6	1,3	1.5	
5	< 0.05	0.05	< 0.05	< 0.05	0.8	0.8	2.7	1.4	
6	< 0.05	0.05	< 0.05	< 0.05	3.1	2.4	0.5	2.4	
7	< 0.05	0.05	< 0.05	< 0.05	2.6	1.8	0.4	0.8	
8	< 0.05	0.05	< 0.05	< 0.05	4.2	90.0	< 0.05	< 0.05	
9	< 0.05	0.05	< 0.05	< 0.05	2.6	150.0	0.2	0.9	
10	< 0.05	< 0.05	< 0.05	< 0.05	5.5	280.0	0.7	0.2	
11	< 0.05	0.05	< 0.05	< 0.05	5.6	2.6	0.7	0.3	
12	NA	NA	< 0.05	< 0.05	4.7	0.2	0.6	0.3	
13	NA	NA	< 0.05	< 0.05	4.8	0.07	0.6	0.3	
14	NA	NA	< 0.05	< 0.05	49.0	6.1	0.8	0.5	
15	NA	NA	< 0.05	< 0.05	9.7	48.0	0.7	0.6	

⁽¹⁾ The probes were installed in water from Tower 9409-10. As a result of the cleansing action of C-CDI, there were considerable fouling products being carried in the water. These deposits accumulated on the probes and the results were readings which were not indicative of the true corrosion inhibitation qualities of C-CDI.

to boil samples on a hot plate by the utility operator, but this step was considered to be a safety hazard in the small water treatment facilities provided.

Environmental Creek Impact

Composite sampling and analyses of the New Hope Pond during the water-treatment evaluation indicated the nonchromate water treatments tested had no environmental impact. However, the significant reduction of chromate, acid, and phenol treatments normally discharging to New Hope Pond from the cooling towers had a significant two-fold impact. The first impact was that the New Hope Pond influent and effluent total chromium during the evaluation was below the 0.05 ppm level established by the EPA and State of Tennessee. This achievement made it possible for the plant to comply with the EPA discharge limits.

The second impact to New Hope Pond is that algae growth has shown a significant increase due to the low chromate level. This increase in algae growth has resulted in variances in the range of pH from 6.5 - 8.5 that have been established as effluent limits. The pH variances have been on the high side (basic pH) and occurred during the summer and early autumn months. Algae, which utilizes sunlight in its growth cycle, produces hydroxyl ions, resulting in a daily-cyclic effect. Peak pH values usually occur in the late evening and early morning hours.

Chromate is toxic to algae; and, when chromate was present in the water, the algae growth was minimal. The result was that the cyclic rise of pH values was substantially depressed, although evident to some degree. This cyclic rise is depicted in Figure 15, which gives the

Table 8
BACTERIA ANALYSES OF COOLING TOWER WATER

Microbiocide Used	Dosage	Date	Total Bacteria Count (cts/ml)	Presence of Sulfate- Reducing Bacteria?
	Tower 9409-22	109-22		
A-MB1 & A-MB2	Both Microbiocides at 50 ppm, Once Each Week	5/28/74	106 - 107	>
A-MB1 & A-MB2	Both Microbiocides at 50 ppm, Once Each Week	5/29/74	106 - 107	Sa - X
A-MB1 & A-MB2	Both Microbiocides at 50 ppm, Once Each Week	6/11/74	105 - 106	Y es
A-MB1 & A-MB2	Both Microbiocides at 50 ppm. Once Each Week	VC/C1/3	-01 - 01	sa i
A-MR1 & A-MR2	D-MB2 at 50 ppm, Once Every Two Weeks	ħ//71/0	, ni - 201	Yes
D-MB1 & D-MB2	D-MB1 at 15 ppm, 3 Times Every Two Weeks	7/11/74	103 - 104	Yes
	D-MB2 at 50 ppm, Once Every Two Weeks	1	400 500	Ç.
C-MB	100 ppm, Once Each Week	6/03/74	10 10.	2
W.C.	100 ppm, Once Each Week	6/05/74	$10^2 \cdot 10^3$	0 2
SW-C	100 ppm, Once Each Week	6/07/74	$10^{2} - 10^{3}$	Yes
97	100 ppm, Once Each Week	10/01/74	104 - 105	Yes
0 C	100 ppm, Once Each Mosk	6/17/74	104 - 105	No
ָרָיאַנּ <u>ש</u>	100 ppin, Once Each Week	6/19/74	105 - 106	No
-MB	100 ppin, Once cacil week	6/21/74		Yes
C-MB	100 ppm, Once Each Week	6/24/74	103 - 104	No
C-MB	100 ppm, Once Each Week	F/1/2/10	102 - 103	Yes
B-MB	40 ppm, Inree Times a week	111716	102 - 103	S _S
B-MB	40 ppm, Three Times a Week	P1 /27 /0	103 - 104	c Z
B-MB	40 ppm, Three Times a Week	1//11/9	10.	Z
B-MB	40 ppm, Three Times a Week	6/12//4	.01 - 201	2
B-MB	40 ppm, Three Times a Week	6/13/74	102 - 103	2 :
B-MB	40 ppm, Two Times a Week	10/09/74	103 - 104	021
B-M8	40 ppm, Two Times a Week	10/12/74	103 - 104	0 :
1 E E	40 ppm, Three Times a Week	5/21/74	106 - 107	o Z
B-MB	40 ppm. Three Times a Week	5/22/74	103 - 104	Yes
B-MB	40 npm Three Times a Week	5/23/74	103 - 104	Yes
aw a	40 nom Three Times a Week	5/24/74	104 - 105	Yes
200	AO COM Three Times a Week	6/06/74	102 - 103	So
0-1/10	40 ppm, filled filled Week	7/09/74	103 - 104	Yes
givi-q	40 Mines Times a Wook	7/11/7	103 - 104	<u>8</u>
B-MB	40 ppin, tilles tilles a Week	6/06/74	101 - 102	No
B-MB	40 ppm, Inree Times a Week	0,00,74	101 - 102	0 <u>2</u>
B-MB	40 ppm, Three Times a Week	6/25/14	10: -10-	. Z
B-MB	40 ppm, Three Times Each Week	6/27/74	102 : 100	2
B-MB	40 ppm, Two Times Each Week	10/02/74	101 - 201	2 3
B-MB	40 ppm, Two Times Each Week	10/09/74	102 - 103	20-

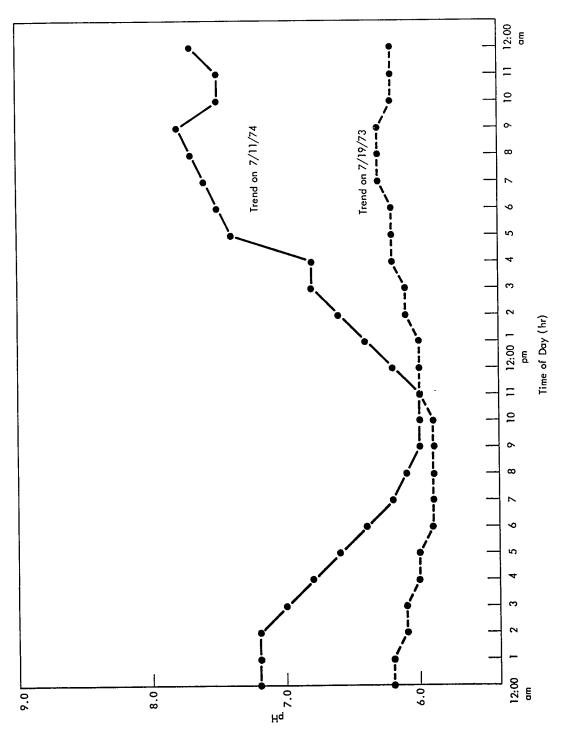


Figure 15. ANALYSIS OF THE NEW HOPE POND EFFLUENT.

pH values on a typical summer day in 1973 when chromate was present in the water, and in 1974 when the chromate level was substantially decreased during the water-treatment evaluation study. The cyclic effect can be observed from these data.

Analysis of Cost

Although many of the cooling towers in the Plant are operated continuously, they are not fully loaded to design conditions (maximum water flow, $10^{\rm O}$ F \triangle T heat load). Several towers are either shut down or the water circulated through the system and bypassed directly to the basin without utilizing the cooling tower.

Taking these factors into consideration, the average annual cost of the water treatment program is as reported in Table 9.

The chromate-based water-treatment program in CY 1973 cost approximately \$37,000. This total does not reflect the cost of filling and delivering approximately 3600 acid carboys nor the cost incurred in maintaining a pH control and recording system at each cooling tower.

-	Table 9	
COOLING TOWE	R TREATM	ENT COST
Microbiocides	в-мв	\$19,800
	C-MB	\$19,800
Inhibitors	B-CDI	\$ 7,900
	C-CDI	\$ 8,500
Total		\$56,000

Recommendations

Corrosion rates from all materials evaluated were satisfactory. Two microbiocide formulations were found to control, satisfactorily, microbiological organisms; however, certain microorganisms were found to become acclimated even to these materials with time. By interchanging these treatments in a heavily infected system, there is a tendency to "shock" the microorganisms and bring them under control.

The following recommendations are offered as a result of this study:

- 1. Maintain B-MB, B-CDI and C-MB, and C-CDI water-treatment systems in the cooling-water systems. Both treatments are necessary due to acclimation of the microorganisms.
- 2. Convert all remaining towers on chromate treatment to the nonchromate treatments.
- 3. Perform minimum biological evaluations on all systems in service during the summer months on a biweekly basis; at all other times, on a monthly basis.
- 4. Operating procedures, which have been prepared for these treatments in each system, should be utilized. A quality assurance program should be established to assure compliance with the established procedures.

ACKNOWLEDGEMENTS

The authors wish to express appreciation to the Phillips Petroleum Company, Sweeney, Texas, and the Exxon Refinery, Baton Rouge, Louisiana, for providing suggested guidelines to establish this water-treatment evaluation program.

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United States Atomic Energy Commission Oak Ridge Operations Post Office Box E Oak Ridge, Tennessee 37830

Attention: Mr. H. D. Hickman

Gentlemen:

The Abatement of Chromate from New Hope Pond, Oak Ridge, Y-12 Plant

Reference is made to letter dated December 11, 1973, on the above subject concerning the plan for abatement of chromate water treatment from the Y-12 Plant cooling towers.

Beginning in January, 1974, a total of sixteen (16) cooling tower water treatment systems were converted to non-chromate treatments, as outlined in the evaluation plan. There have been six (6) cooling tower water treatment systems that have remained on the chromate treatment.

Since January, 1974, the effluent of New Hope Pond has been analyzed to determine the effect of the water treatment changeover. The non-chromate water treatment program has resulted in the New Hope Pond effluent meeting the present environmental requirements for discharge with respect to the chromate, phosphorus and zinc levels. A recent audit by the ORO-AEC Environmental Control Division has further indicated that all requirements have been met.

The water treatment evaluation program is indicating very satisfactory results. Corrosion rates, heat transfer data, microbiological control, field and laboratory analysis, and control of materials are well within acceptable limits. The following is a result of the program:

- Five of the six cooling tower water treatment systems remaining on chromate treatment will be changed over to non-chromate as soon as the present heat load season is over. It is planned that only one cooling tower will remain on chromate treatment. This tower serves the Nitrogen Liquefication Plant, which has exceptionally high metal temperatures. The blowdown from this system is normally 2 - 3 qpm.
- 2. A cost comparison between the chromate water treatment program and the non-chromate program, which meets EPA requirements for discharge, indicates the following:

- a. Cost of chromate treatment/1000 gallons blowdown water = \$0.19
 (Does not include filling, handling and storage of sulfuric acid carboys.)
- b. Cost of non-chromate treatment/1000 gallons blowdown water = \$0.28
- 3. The microbicide treatment is applied as a shock treatment on a weekly basis and indicates the following:
 - a. Cost of phenate treatment/1000 gallons water in a system = \$0.25
 - b. Cost of biodegradable microbicide/1000 gallons water in a system = \$0.50
- 4. Distribution basin covers of noncombustible cement asbestos board are being installed on eleven crossflow type cooling towers. Water basin covers of prestressed concrete span-deck are being installed on two of the cooling tower water basins. These covers exclude the sunlight which causes excessive growth of algae on the decks and in the basins and will result in a significant decrease in microbicide demand in the control of microbiological growth.
- 5. The evaluation program will be terminated October, 1974, with selection of one of the four water treatment programs being evaluated.

If any questions arise pertaining to the water treatment evaluation program, please contact me at your earliest convenience.

Very truly yours,

J. M. Case, Superintendent
Oak Ridge Y-12 Plant

JRD:dc

cc: R. F. Hibbs

P. R. Vanstrum

C. J. Parks

G. W. Evans

C. C. Hopkins

G. R. Jasny

R. G. Jordan

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W. J. Wilcox, Jr. ← «««

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